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(54) **Process, Coating and Device for the Manufacture of Coated Glass Hollowware.**

(57) Process for the manufacture of coated glass hollowware by application of a radical-polymerizable coating and subsequent curing of the formed coating with high-energy radiation, characterized by the fact that it is carried out on-line, wherein the glass hollowware obtained from a glass melt is subjected to a cold end coating, sorted and then immediately coated with a solvent-free, radical-polymerizable and/or cation-polymerizable coating to a coating thickness of at least 8 μm , whereupon the formed coating is cured by high-energy radiation and then exposed to a stream of air.

The process is applicable in the manufacture of bottles having a protective surface film and decorated bottles.

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The invention involves the manufacture of coated glass hollowware, especially glass hollowware open on one side, such as glass containers and glass bottles, by application of a radical-polymerizable and/or cation-polymerizable coating and subsequent curing of the formed coating by means of high-energy radiation.

5 During the manufacture of glass bottles or glass containers, some of the manufactured objects have scorings and weak points that do not have the conventionally required minimum internal pressure strength of 16-18 bar. For strongly carbon dioxide-containing beverages, such as, for example, champagne, glass bottles can easily be strained above this minimum pressure limit, so that they can easily explode at the least strain if the minimum requirement is not satisfied. Since it cannot be
10 completely ruled out that such objects leave production without being detected despite random sample control, this phenomenon results in a corresponding breakage potential when the containers are filled with beverages under pressure (e.g. champagne) in the filling section. However, the greatest danger is due to a small percentage of glass bottles that pass inspection and are put on the market at barely above the minimum pressure strength despite previous selection, where they quickly fall below the
15 minimum pressure strength due to extreme strain on the glass bottles.

As a rule, highly pressure-strained bottles, such as e.g. 0.75 L champagne bottles, have a mean internal pressure strength of about 20-30 bar. Although glass is one of the hardest and most brittle materials, its surface is generally susceptible to damage. Damage occurs on the market or with the consumer, in storage or in handling, during which the surface of glass bottles can be damaged with
20 cracks or scratches by mechanical scoring, for example by grains of sand. Such scorings that occur in practice can be simulated with a so-called single liner test, in which several bottles filled to their intrinsic weight rub against each other while rotating over a certain period of time. With this test the cold end coating materials currently used in conventional bottle manufacturing, such as, for example, bottles coated with polyethylene dispersions, surfactants, waxes etc. can very easily incur a
25 corresponding surface scoring so that their internal pressure stability falls to values below the minimum requirements.

Bottles damaged in such a way represent the greatest potential for danger to the consumer. In order to eliminate, for the most part, scorings of this type, e.g. champagne bottles are manufactured due to safety reasons with a corresponding wall thickness on the part of the glass manufacturer, who
30 makes allowance for the higher weight of the bottles in order to ensure a minimum scoring risk.

Today there is an increasing demand for decorations on glass bottles and glass containers, on the one hand by the consumer, on the other by the marketing end of the seller. In many areas filling sections demand a certain tint of the glass bottles or glass containers as an unrecognizable trademark, with which they put their products on the market. For the glass melt in the area of the so-called feeder,
35 glass bottles are typically tinted with a special tint. In contrast to the conventional brown and green tints, this procedure allows the manufacture, to a limited extent, of special dark to light brown and green tints, in part also blue tints. Other tints, such as, for example, yellow to orange tints, which are typical for light bulbs, cannot be manufactured for glass bottles, since such tintings are obtained in part with highly toxic salts such as cadmium salts. The tinting of glass with other tints, such as e.g. deep-
40 dark blue or red, can likewise be obtained only with toxicologically harmful heavy metal salts (cobalt) or very expensive additives (gold).

Therefore, in the literature, protective and decorative coatings are described for glass containers, such as glass bottles, and used in practice; one example of a decorative application is the so-called plasti-shield process, in which a film of polyvinyl chloride or polystyrene is shrunk around bottles. Glass
45 bottles provided with plastic coatings have also been described, whereby the requirement was also described of applying such plastic coatings on-line immediately after the manufacture of the glass bottles. The international patent applications WO 90/05031 and WO 90/05088 describe the manufacture of transparent coatings on glass containers, which are intended to produce a high luster and abrasion resistance. Before the transparent coatings are applied, inscriptions and labels can be
50 applied to the glass containers, which inscriptions and labels are protected by the coatings. Solvent-containing varnishes that can be cured by ultraviolet radiation and are based on acrylics are used as coating materials. These varnishes are sprayed on, the solvent is vaporized and the remaining coating is cured by ultraviolet light.

The known processes for the manufacture of a scratch or chip protection in the manufacture of a decorative surface could until now be carried out only in the off-line operation. An on-line production
55 could not be used in practice. The on-line production includes the manufacture of a high number of bottles, for example 200 to 300 bottles/min, i.e. about 3 to 5 bottles/sec. Until now no practically

useful technology was available that made it possible to provide glass hollowware, such as glass bottles or glass containers, with organic coatings on-line at such high production rates in order to produce a glass/plastic composite.

5 The purpose of the invention is therefore to make available a process for the manufacture of coated glass hollowware, such as glass bottles and glass containers, that can be adapted to the current manufacturing processes for glass hollowware with respect to apparatus and space and results in glass hollowware having mechanically and chemically more stable, decorative and odor-free surfaces at high production rates.

10 It has been shown that this purpose can be realized by a process, which represents one topic of the invention, in which the glass hollowware produced from a glass melt is subjected to a cold end coating, sorted and then immediately coated with a solvent-free radical-polymerizable and/or cation-polymerizable coating at a coating thickness of at least 8 μm , preferably at least 10 μm , on-line or in series, whereupon the formed coating is cured by high-energy radiation and then exposed to a stream of air.

15 The coating process in accordance with the invention can be carried out in association with the otherwise conventional manufacture of glass hollowware, such as glass bottles and glass containers. The glass hollowware is produced from a glass melt using the method familiar to the expert, optionally provided with a hot end coating, cooled and then subjected to a cold end coating.

20 The hot end coating can be carried out in the conventional manner of bottle manufacturing, for example by treatment with titanium compounds such as titanium tetrachloride or tin compounds such as tin organyl compounds or stannic chloride. The hot end coating is carried out to correct microcracks that can arise in the forming process.

In association with the possible hot end coating, the glass hollowware is generally fed to a cooling oven, after which a so-called cold end coating is applied.

25 The cold end coating generally functions as an antislip protection for the glass hollowware that is once again fed to the sorting line for physical quality assurance and random sample quality control. Antislip agents that are used include, for example, polyethylene dispersions or surfactants, which are intended to prevent intense friction of the glass articles against each other and thus any possibility of external damage.

30 In practice the sorting line is followed by palletization or packing of the glass hollowware, which is then immediately forwarded to shipping.

35 In accordance with the invention the sorting line is followed by an on-line coating with subsequent air-blasting, which is optionally followed by an additional control of the appearance of the coating (luster, flow etc.), the hardness, the coating thickness, the odor and other properties of the produced glass hollowware, which can then be palletized and prepared for shipping.

40 In accordance with a preferred embodiment of the invention, the cold end coating is carried out by application of polyalkene glycol fatty acid esters, wherein the alkene groups preferably have 2 to 4 carbon atoms. The fatty acids on which the esters are based are preferably higher fatty acids having for example 7 to 22 carbons atoms, such as capric acid, caprylic acid, lauric acid, myristic acid, behenic acid, arachidic acid and, preferred due to cost reasons, palmitic acid and stearic acid, whereby such acids are generally present in a mixture. Such esters can be obtained commercially. Usable commercial products are, for example, polyethylene glycol fatty acids of a mixture of the fatty acids listed above as examples, wherein, for example, the content of palmitic acid is about 40 to 55 %wt. and that of stearic acid is likewise about 40 to 55 %wt. (in relation to the fatty acid content).

45 In accordance with a preferred embodiment the preferred cold end coating material in accordance with the invention based on the fatty acid esters described above can be modified by the addition of silanes, especially of one or more alkoxyl silanes. Such silanes preferably have glycidyl groups; examples are γ -glycidyloxypropyl trimethoxysilane and γ -glycidyloxypropyl triethoxysilane. The amount ratio of fatty acid ester/silane can vary from 100:10 to 100:1 in relation to the solid weight of the modified cold end coating material.

50 The cold end coating material is generally sprayed on the obtained glass hollowware in aqueous solution, for example with a solid content of 1 to 10 %wt., preferably 2 to 5 %wt., in the conventional installation in the glassworks. These solutions generally have temperatures of 100 to 130°C so that the water is vaporized and a film of the fatty acid esters remains on the surfaces of the glass hollowware as a temporary antislip protection.

55 In a surprising manner it was shown in accordance with the invention that this fatty acid ester film, which optionally contains silanes, can serve as an adhesion improving agent between the glass

substrate and the curable coating that is later applied by high-energy radiation, and moreover contributes to the improvement of the water resistance (the latter especially when silanes are added).

In association with the cold end coating the glass articles produced by the process in accordance with the invention can be subjected to a conventional sorting, whereby the fatty acid ester film serves as a lubricant.

After the sorting the glass hollowware having the cold end coating is coated with a solvent-free, radical-polymerizable or cation-polymerizable coating material.

Conventional polymerizable or curable monomers, oligomers and/or polymers that can be polymerized by high-energy radiation and especially preferred by UV radiation can be used as radical-polymerizable coating materials. Such radiation-curable monomers, oligomers and polymers are familiar to the expert. They are used alone or in mixture, whereby it should be noted that they have such a viscosity that an application in the liquid state is possible without the addition of solvent. The application can be carried out in a conventional manner, for example by rolling, immersion or felting. However, spray coating is preferred due to the high speeds. The coating material compositions are preferably selected so that a suitable viscosity for the spray application is present, for example a viscosity of 15 to 40, preferably 16 to 25 seconds at room temperature, measured in the Ford cup, DIN 4 mm.

Examples of radical-polymerizable coating materials, especially coating materials curable by UV radiation, are monomers, oligomers, polymers, copolymers or combinations thereof, having one or more olefinic double bonds, for example acrylate and methacrylate. They can be monofunctional, difunctional, trifunctional and polyfunctional. Examples are butyl(meth)acrylate, dipropylene glycol di(meth)acrylate, tripropylene glycol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, pentaerythritol tetra(meth)acrylate. Examples of oligomers are (meth)acrylic-functional (meth)acrylic copolymers, epoxide resin (meth)acrylates such as ethylene oxide/propylene oxide trimethylolpropane triacrylate (for example having a molecular weight of 480); polyester polyols, functionalized with (meth)acrylic acid; melamines such as hexamethoxymethyl melamine, partially etherized with hydroxyalkyl(meth)acrylates; methanes of polyols, converted with (especially aliphatic) diisocyanate hydroxyalkyl(meth)acrylate adducts. The term (meth)acrylate used here and hereafter means acrylates and/or methacrylates. The coatings, in addition to the radical-curable monomers, oligomers and polymers, can also contain resins soluble in these substances, for example silicone resin, which in such forms are not subject to radiation curing. They are incorporated in the coating during the curing of the radiation-curable components. The addition of silicone resins is especially preferred, particularly the addition of methyl phenyl silicone resins, such as, for example, the commercial product REN 60, Wacker-Chemie. If such resins are obtained dissolved in a solvent, the solvent is replaced by a radiation-curable monomer, for example a di(meth)acrylate such as dipropylene glycol diacrylate. For this purpose a solution of the silicone resin is combined with the acrylate, after which the solvent can be quantitatively distilled off.

The radical-polymerizable coatings that can be used for the process in accordance with the invention can also contain coupling agents in accordance with a preferred embodiment. Examples of suitable coupling agents are organofunctional silanes, especially silanes that contain glycidyl groups. Especially preferred examples are 3-glycidyloxypropyl trimethoxysilane and 3-glycidyloxypropyl triethoxysilane, whereby the latter is especially preferred. Such coupling agents can be contained, for example, in amounts of 1 to 10 %wt. in relation to the coating composition.

Since the coating materials that can be used in accordance with the invention are intended to be curable by radiation, in particular by UV radiation, they preferably contain photoinitiators. Such photoinitiators can be contained, for example, in amounts from 2 to 10 %wt. Conventional photoinitiators are suitable as photoinitiators, as they are common in the area of radical-curable coating compositions by UV radiation.

Examples of photoinitiators that can be used in accordance with the invention for radical polymerization, and which are common in the field of curable compositions by high-energy radiation, are those that absorb, for example, in the wavelength range from 190 to 400 nm. Examples of these are conventional organic peroxides and azo compounds. Examples of peroxides are di-t-butyl peroxide, dibenzoyl peroxide, peroxycarboxylic acids such as peroxyacetic acid, peroxodicarbonates such as di-sec-butyl-peroxodicarbonate, peroxide ethers such as 2-ethyl hexanoic acid-tert-butyl perester, hydroperoxides such as cumene peroxide and ketone peroxides such as methyl ethyl ketone peroxide. An example of an azo initiator is azo bis-isobutyronitrile. Additional examples of photoinitiators are chlorine-containing initiators such as chlorine-containing aromatic compounds, e.g. described in US-A-

4,089,815; aromatic ketones as described in US-A-4,318,791 or EP-A-0 003 002 and EP-A-0 161 463; hydroxyalkyl phenones as described in US-A-4,347,111; phosphine oxides as described in EP-A-0 007 086, 0 007 508 and 0 304 783; initiators based on hydroxyalkyl phenones as described in US-A-4,602,097, unsaturated initiators such as OH-functional aromatic compounds that have been esterified, for example, with acrylic acid as described in US-A-3,929,490, EP-A-0 143 201 and 0 341 560; or combinations of such initiators as described, for example, in US-A-4,017,652. Photoinitiators of the acyl phosphane oxide type and of the bis-acyl phosphane oxide type are also favorably used, as they are described, for example, in EP-A-0 413 657. They are, optionally in combination with other photoinitiators such as, for example, of the hydroxyalkyl phenone type, especially suitable for color coatings that are pigmented from transparent to opaque. A preferred example of photoinitiators of the hydroxyalkyl phenone type is 1-hydroxy-2-methyl-2-phenyl-propan-2-one.

In accordance with a preferred embodiment the invention involves radical-polymerizable coatings that can be used especially for coating glass, e.g. glass hollowware in the on-line and off-line processes, e.g. for the process in accordance with the invention. Such preferred coatings contain

A) 1 to 10 %wt. of one or more silanes, especially glycidyl group-containing silanes as coupling agents, for example 3-glycidyloxypropyl trimethoxysilane and preferably 3-glycidyloxypropyl triethoxysilane.

B) 1 to 10 %wt. of one or more monophosphates of hydroxyalkyl(meth)acrylates, whereby the alkyl groups preferably contain 1 to 4 carbon atoms and preferably represent the ethyl group,

C) 2 to 10 %wt. of one or more photoinitiators, whereby those of the hydroxyalkyl or hydroxycycloalkyl phenone types are preferred; and

D) the remainder to 100 %wt. di(meth)acrylates, tri(meth)acrylates and/or higher functional (meth)acrylates in the form of monomers, oligomers and/or polymers, optionally together with mono(meth)acrylates and/or silicone resins, whereby the preceding components A) to D) add up to 100 %wt., as well as

E) optionally additional conventional varnish additives, dyes and/or pigments.

The parts by amount of low and high-molecular components are thereby selected so that the total composition has spray viscosity.

In accordance with an especially preferred embodiment of the invention, the coating contains, in addition to the above-mentioned components A), B) and C) in the given amounts, 5 to 30 %wt. of one or more nonradiation-curable silicone resins dissolved in the other components, and as the remainder to 100 %wt. one or more di, tri, tetra(meth)acrylates and/or higher functional (meth)acrylates, whereby the above components add up to 100 %wt., as well as optionally additional E) conventional varnish additives, dyes and/or pigments.

Preferably the nonradiation-curable silicone resins have reactive hydrogen atoms, such as, for example, hydroxyl groups.

The silicone resin preferably involves a methyl phenyl silicone resin that is commercially available, for example under the trade name REN 60. Such silicone resins are generally present in dissolved form, for example, dissolved in xylene and/or toluene. The concentration in the solution is generally in the order of magnitude of about 60 %wt. In accordance with the invention the solvent is replaced by an unsaturated, radical-polymerizable monomer that dissolves the silicone resin, such as, for example, preferably dipropylene glycol diacrylate. This can take place by mixing the solution with dipropylene glycol diacrylate and distilling off the solvent. As an example, a solution of the methyl phenyl silicone resin in dipropylene glycol diacrylate can thus be prepared in the weight ratio of about 60:40.

In accordance with the above-mentioned especially preferred embodiment, the remainder to 100 %wt. can consist, for example, of an ethylene oxide/propylene oxide trimethylolpropane triacrylate (an oligomer having a molecular weight in the order of magnitude of 480), tripropylene glycol diacrylate, dipropylene glycol diacrylate, trimethylolpropane triacrylate, pentaerythritol tetraacrylate or mixtures thereof.

In accordance with an additional especially preferred embodiment, the coating used in accordance with the invention contains, in addition to the above-mentioned components A), B) and C) in the above-given parts by amount, 5 to 40 %wt. of one or more di(meth)acrylates, 5 to 40 %wt. of one or more tri and/or polyfunctional (meth)acrylates and 0 to 20 %wt. of one or more mono(meth)acrylates, as well as optionally additional conventional varnish additives. Especially preferred examples of monofunctional acrylates that can be used in this embodiment are isobornyl, phenoxyethyl, tetrahydrofuran, octyl, dicyclopentenyl and decylacrylate, which can also be replaced in part or in whole by other monomers

such as N-vinyl pyrrolidone. For this embodiment, especially preferred examples of diacrylates are hexanediol diacrylate, dipropylene glycol diacrylate, tripropylene glycol diacrylate, bisphenol-A-diacrylate, as well as hydroxyalkyl acrylates monoesterified with phosphoric acid. For this preferred embodiment, especially preferred examples of tri and polyfunctional acrylates are trimethylolpropane triacrylate, ethylene oxide propylene oxide trimethylolpropane triacrylate (oligomer having a molecular weight of about 480), pentaerythritol tetraacrylate as well as polyfunctional phosphates of hydroxyalkyl acrylates; polyester acrylates involving, for example, saturated polyesters from mixtures of multivalent polyalcohols and dicarboxylic acids such as adipic acid, which are functionalized with acrylic acid; acrylic-functional melamines such as hexamethoxymethyl melamine, partially etherized with hydroxyacrylates; conversion products of hydroxyacrylates with dicarboxylic anhydrides, for example mixtures of dicarboxylic anhydrides such as phthalic anhydride, tetrahydrophthalic anhydride and/or succinic anhydride; cycloaliphatic and aliphatic epoxide acrylates, optionally in mixture; as well as polyurethane-modified acrylates. For the manufacture of such coating agents containing higher-molecular materials, liquid monomers are mixed with higher-viscosity, higher-molecular portions in such amounts that spray application is achieved; i.e., for example a viscosity of 15-40 seconds discharge time at room temperature in the DIN 4 mm Ford cup is attained.

For the process in accordance with the invention, solvent-free, cation-polymerizable coating agents can also be used in addition to solvent-free, radical-polymerizable coating agents. The coating agents can also consist of mixtures of solvent-free radical and cation-polymerizable coating agents.

Solvent-free coating agent compositions that contain components polymerizable via high-energy radiation and preferably UV radiation can be used as cation-polymerizable coating agents. Especially suitable components for such coating agents are, for example, those that contain a mixture of components containing epoxide groups and hydroxyl groups. The compounds containing epoxide groups have at least two epoxide groups per molecule; however, they can also contain three or more epoxide groups per molecule. In the same manner the components that can be used as hydroxyl groups are at least difunctional; however, components having three or more hydroxyl groups per molecule can also be used.

The components containing epoxide groups and hydroxyl groups can involve monomeric, oligomeric or polymeric compounds. The molecular weights used in this process play no role, as also in the case of the above-mentioned radical-polymerizable components; the mixtures must merely be chosen so that suitable viscosities of the total mixture are attained per application, especially for the spray application.

Examples of usable di and polyepoxides are those based on cycloaliphatic diepoxides such as 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, such as the commercial products Cyacure UVR 6110, Union Carbide, or Degacure K 126, Degussa.

Additional examples of epoxide resins having two or more epoxide groups per molecule are those based on bisphenol A, such as the commercial products Epicote 828, Shell AG, DER 331, Dow, and Beckopox EP 138, Hoechst AG.

Low-molecular monomers can also be used, for example diglycidyl ethers such as hexanediol diglycidyl ether or butanediol diglycidyl ether. Such diglycidyl ethers can be particularly used as reactive thinning agents for the dissolution of high-molecular products.

Examples of polyol compounds that can be used include di, tri and also polyfunctional higher and lower-molecular polyols, whereby such polyols can be homo and copolymerizates such as, for example, polyether polyols or addition products of polyols to diepoxides, for example the cycloaliphatic diepoxides previously mentioned as examples. Special examples of usable homopolymerizates are polycaprolactone polyols, di and trifunctional, such as the commercial product Tone 0301, Union Carbide. Examples of addition products are those of polyols, such as the above-mentioned polycaprolactone polyols to diepoxides, for example the above-mentioned alicyclic diepoxides such as the commercial products Cyacure UVR 6379 and 6351. Through the selection of higher or lower-molecular polyols, the flexibility of the epoxides thereby reacting in the coating can be influenced; such polyols are therefore frequently designated as flexibilizers.

Copolymers can also be incorporated in the cation-polymerizable coatings usable in accordance with the invention, which copolymers are usually not curable with radiation, such as, for example, copolymers based on styrene having olefinic monomers, whereby the latter can also contain functional groups such as hydroxyl groups; a preferred example of olefinically unsaturated comonomers is allyl alcohol. An OH-functional copolymer of styrene allyl alcohol having an OH number of 188 is preferably used, such as, for example, the commercial product RJ 100, Monsanto. Such copolymers are incorporated in the formed coating during the curing of the cation-curable coating.

Photoinitiators are added to the cationic coatings curable via radiation used in accordance with the invention, which photoinitiators are typical for the cationic polymerization initiated by radiation and are familiar to the expert. Such photoinitiators are used in conventional amounts. Examples are triarylsulfonium salts such as triarylsulfonium hexafluorophosphate and triarylsulfonium hexafluoroantimonate, η^5 -2,4-cyclopentadien-1-yl[(1,2,3,4,5,6- η)-(1-methylethyl)benzene]-iron(1+)-hexafluorophosphate(1-).

The photoinitiators can be used alone or in mixture.

In accordance with a preferred embodiment, the cation-polymerizable coatings usable in accordance with the invention can also contain coupling agents. Examples are organofunctional silanes, as they have already been described as examples for use in the radical-polymerizable coatings.

The coatings used in accordance with the invention based on radical-polymerizable and/or cation-polymerizable bonding agents can be combined with conventional varnish additives, such as, for example, slip additives (lubricants), defoaming agents, flow control agents and/or UV absorbers. This process involves conventional products familiar to the expert. Silicone oils, as an example, can be used as flow control agents. The coatings used in accordance with the invention can also contain pigments and/or dyes. This can involve for example transparent pigments and/or opaque pigments as well as transparent and/or opaque dyes.

Such additives, pigments and/or dyes are added in such amounts that will not impair the radiation hardenability of the coatings.

In accordance with a preferred embodiment, the cation-polymerizable coatings that can be used in accordance with the invention contain 10 to 80 %wt. of one or more epoxide resins based on cycloaliphatic diepoxides containing at least two epoxide groups per molecule;

5 to 50 %wt. of one or more liquid polyols having at least two hydroxyl groups per molecule as flexibilizer;

5 to 50 %wt. of one or more liquid diglycidyl ether as reactive thinning agent;

5 to 30 %wt. of one or more epoxide resins based on bisphenol A;

0-20 %wt., preferably 1 to 20 %wt. of one or more copolymers of styrene having α,β -olefinically unsaturated monomers, especially allyl alcohol;

1 to 5 %wt. of one or more photoinitiators and

1 to 5 %wt. of one or more silanes, preferably glycidyl group-containing silanes, wherein the preceding components add up to 100 %wt. Conventional varnish additives, dyes and/or pigments can be added to the composition.

For the process in accordance with the invention, the coating agents that can be polymerized by high-energy radiation are preferably applied by spray application to the glass hollowware coated with the cold end coating agent. The coating thickness is at least 8 μm , preferably at least 10 μm and especially preferably at least 15 μm in relation to the dry film strength obtained after curing. The glass hollowware that will be coated preferably has temperatures of for example 25 to 70°C, especially preferably from 50 to 70°C. In case such temperatures are no longer present after the cold end coating and sorting, the glass hollowware that will be coated can be subjected to a preheating, for example with a nozzle dryer.

The spraying procedure is carried out for the process in accordance with the invention preferably without use of a protection gas. The latter, for example nitrogen, is frequently necessary in known processes for obtaining thinner coating thicknesses.

The spraying procedure is preferably carried out in an encapsulated spraying device which is thereby protected from dust, whereby the obtained overspray is preferably recycled. This can take place, for example, by catching the overspray in a wet irrigation that consists of the coating agent. The mixture of overspray and coating agent drawn off from the chamber can optionally be fed back to the wet spraying and/or spraying device over a filter.

The coated glass hollowware exiting the coating zone, for example the spray chamber, is then immediately cured by high-energy radiation, for example UV radiation. This can take place in a curing zone following the coating zone, for example a UV drying chamber, where the coated glass articles pass by one or more radiation devices, such as UV emitters. Such emitters preferably have a power of 80-240 W per cm (emitter length).

For the process in accordance with the invention, after the curing by high-energy radiation the coated glass hollowware is subjected to a heat treatment, which results in a second curing as well as in an extensive removal of the odor. The heat treatment is carried out by air-blasting with hot air of about 100 to 400°C, preferably 200 to 300°C, for about 5 to 30, preferably 5 to 10 seconds. As

examples, a circulating oven or a conventional nozzle dryer are suitable for this purpose.

After the above-described heat treatment the coated glass hollowware exiting the curing zone can optionally be exposed to a stream of cold air (around room temperature in the order of magnitude of 15 to 25°C), until it has attained a temperature of about 40°C or below. This air-blasting makes it possible to remove any undesired odors so that the coated material can be immediately forwarded to palletizing and optionally packing with subsequent shipping.

The process in accordance with the invention is preferably carried out with a device that immediately follows the conventional manufacture of glass hollowware, such as bottles, with subsequent cold end coating.

The process in accordance with the invention can be carried out on-line in association with the manufacture of glass hollowware and its cold end coating. After the cold end coating the bottles are transported further in a conventional manner, for example with a conveyor belt, during which the bottles come in contact with each other. Prior to the coating the bottles are first isolated. This can take place in a conventional manner, for example by pick-up in a screw, which separates the glass bottles from each other, and subsequent separation with a star wheel. The glass hollowware, for example the bottles, is then preferably picked up at the upper open end by a gripping device and fed suspended in this position to the spraying device.

The parts of the gripping device in contact with the glass are preferably constructed of a metal-free, high temperature-resistant material, for example of Teflon, polyamides, and/or polyphenylene sulfide. The gripper is preferably protected from spray mists by a stencil (matrix). The stencil can be designed so that it is adjustable in order to prevent spray mists from entering or contacting the mouth area of the glass hollowware or bottles. The gripping devices are constructed so that the glass hollowware can be introduced to the spray zone suspended from the top. For example, the gripping devices can be mounted on chain conveyors.

A heating device, for example a nozzle dryer, can be provided before the glass hollowware is introduced to the spray zone. This heating device functions to preheat glass hollowware that has been strongly cooled to temperatures of 25 to 70°C, preferably 50 to 70°C before it is introduced to the spray zone.

An encapsulated spray booth is preferably used as the spray zone in order to ensure a dust-free operation. Moreover, the spray booth is preferably designed so that no daylight can enter in order to prevent a premature polymerization of the coating materials that are cured by UV radiation. This is especially preferred if overspray is to be caught and recycled. Optionally, the spray booth can be illuminated with UV-free light, for example with yellow light.

The varnish or spray booth can be equipped with one or more, preferably about three spray pistols per object being varnished, which involves moving pistols in series. Stationary pistols can also be provided on lift cradles. The spray process preferably takes place via compressed air or as an airless process. The glass hollowware can be rotated by a friction drive for example at 1 to 10 rotations/sec in order to ensure even varnishing.

The varnish temperature during spraying fluctuates for example from 20 to 50°C.

The spray booths are constructed in accordance with a preferred embodiment of the invention so that recycling the overspray of the coating material is possible. For this purpose the spray booths and the parts in contact with the material are preferably high-grade steel so that corrosion cannot occur and the coating material is not polymerized by the influence of metal. For recycling the overspray the spray booth is equipped with a wet irrigation zone, for example in the form of the back wall of the booth. The sprayed coating material is used as the liquid for irrigating the wet irrigation zone and for the wet separation. This can be fed back together with the overspray to the wet irrigation zone on the one hand and to the spray pistols on the other by ring mains and stubs over one or more pumps and optionally through filters. In this manner the formation of scraps can be prevented and the used solvent-free coating material can be processed at an efficiency of almost 100%.

The wet irrigation zone can be designed in a conventional manner. For example, the booth can be equipped with a vortex washer or with a device for narrowing the air passage, such as for example a Venturi nozzle. In addition, a centrifugal separation can be provided.

In accordance with a preferred embodiment, an additional wet separation is installed behind the vortex washer of the Venturi device. For example, inserts with Raschig rings or other ceramic articles, as well as optionally inserts of additional high-grade steel baffle filter cloths, are located behind the vortex washer of the Venturi device in order to ensure a complete separation of the coating and overspray material from the exhaust air.

In addition, an electrostatic wet filter consisting of plates or rods can then be installed in order to comply with the legal exhaust air requirements.

The coating agent obtained from the wet irrigation zone of the spray booth and containing overspray can be fed back to the wet irrigation in the spray booth as well as to the supply of the spray pistols by ring mains. For this purpose the ring mains are equipped with pumps. Filters are also preferably interposed to remove impurities. Optionally, the coating agent obtained from the wet irrigation zone is first fed over a reservoir, optionally also to degassing. The degassing can take place in the reservoir, for example by ultrasound or by equipment as a subpressure chamber or by run off of the microfoam over a heated run-off plate.

From the spray zone the coated glass hollowware is fed to the radiation curing plant, for example to a UV dryer. In order to obtain a radiation screening, the feeding can take place over a conventional omega loop or deflection.

The radiation takes place with emitters at powers in the order of magnitude from 80 to 240 W/cm, preferably about 200 W/cm. For example, mercury high-pressure emitters, microwave-ignited fusion systems or Excimer lasers can be used. The coated glass articles pass by several emitters, for example 2 to 3 emitters, during which a friction-driven rotation also takes place around each article's own axis. Essentially the production rate is determined by the number of emitters. By using several high-power emitters and the rotation of the glass hollowware, a very compact design of the drying plant can be maintained.

The dryer length can be minimized by placing the emitters in combination opposite each other, so that different areas of the glass hollowware can be irradiated simultaneously.

The glass articles coming from the dryer are fed through a high-temperature aftertreatment zone. In this zone the articles can for example be exposed to a stream of hot air for a short time (for example, a conventional nozzle dryer or circulating oven can be used). The air temperature is, for example, 100 to 400°C, preferably 200 to 400°C, especially preferably 200 to 300°C and the rinsing with this hot air takes place, for example, for 5 to 30 seconds, whereby the glass hollowware can also be rotated. Such a high-temperature aftertreatment results in a superheating of the dried varnish film, whereby fragments consisting of photoinitiator components and degradation products as well as residual monomers can be removed.

Apparatus for blasting the glass hollowware with cold air (room temperature around 15 to 25°C) can then be assigned before and/or after the take-off equipment. The air-blasting takes place until a temperature of the glass hollowware of 40°C or below is attained. This air-blasting removes residual odors from the glass articles so that they can be forwarded immediately to palletization, packing and shipping.

The glass hollowware is removed from the gripping device to a single liner for example with a star, for example before the air-blasting with cold air.

After the coating plant (prior to the drying plant), immediately after the drying plant (prior to the hot air treatment zone, or after the hot air treatment zone) ejectors can be provided, which either prevent defective coated glass hollowware from entering the dryer zone or prevent undried or insufficiently dried glass hollowware from reaching the discharge chutes which would result in impurities.

The attached figure shows an example of a preferred embodiment of the device in accordance with the invention.

In the figure 1 represents the intake (feeding), for example a conveyor belt, coming from the glass hollowware manufacture and cold end coating. [Number] 2 represents a branching, which leads to a second coating device of the same design. Due to safety reasons, in accordance with the invention it is preferred that the coating and curing processes be carried out in the tandem operation T. The glass hollowware is introduced to an encapsulated system over the intake 1 and introduced to the varnishing booth (spray booth) 5 suspended with the opening pointed up over a screw 3 and a star 4. The coating takes place at the spray station 6 by means of spray pistols. The varnishing booth is preferably equipped with a wet irrigation zone 7, which is rinsed with the coating agent. This is recycled to the wet irrigation and to the spray pistols. The coating agent used for the wet irrigation and containing overspray is collected on the floor of the booth and the exhaust air is introduced over a vortex zone or Venturi nozzle in a booth located behind the varnishing booth, where it is drawn off through filter inserts of Raschig rings and optionally filter cloth inserts of high-grade steel, which are not shown in the figure, over a suction fan 8.

The coated glass hollowware is then introduced in a suspended manner over a deflection 9, which functions as radiation protection, to the UV dryer 10, where it passes by several UV emitters 11. The

glass hollowware exiting the UV dryer is fed through a high-temperature aftertreatment plant 12, where it is subjected to, for example, a high-temperature blower, and removed by a star 13 to a single liner 14 (take-off), where an aftertreatment with cold air 15 can take place. The aftertreatment with cold air can also take place immediately after the high-temperature treatment, e.g. prior to the start 13. The glass hollowware is fed further from the closed system to palletization, packing and shipping over the outlet 16. Discharge devices can be provided at the points of the figure marked with A, which devices discharge incompletely or poorly coated glass hollowware or incompletely or undried glass hollowware. Such devices can be controlled by conventional error detection systems.

The invention in question makes available a process that makes possible the coating of glass hollowware, especially bottles, in the on-line process immediately after the manufacture of glass or glass hollowware in practice. The process makes available glass/plastic composites that provide an unexcelled surface protection of glass hollowware. Dangers that result from surface scorings of glass hollowware, especially bottles with a relatively high internal pressure, are thus prevented. It is also possible to manufacture decorative coatings, such as the widest variety of tints, in a reproducible manner. The method in accordance with the invention makes possible a high production rate, for example 200 to 300 bottles per minute. The process in accordance with the invention can be carried out with devices of compact design having no great spatial requirements. The process can be carried out in an environmentally safe manner without solvent emission and is also not dependent on the availability of protection gases such as nitrogen. The use of solvent-free coating systems makes possible a recycling of the coating material at the spray station so that a high efficiency is obtained. One obtains odor-free glass hollowware whose inside is free of contaminants. This is especially important for the manufacture of beverage bottles. The process in accordance with the invention can be especially favorably applied to bottles that are intended to hold beverages having a high carbon dioxide content, such as, for example, soft drink and champagne bottles. The environmental compatibility of the process in accordance with the invention is also increased by the fact that in accordance with a preferred embodiment special cold end coating agents are used, which do not have to be removed prior to the coating.

The following examples illustrate the preferred usable coating compositions in accordance with the invention.

Manufacture of solvent-free coating compositions having a content of silicone resins that are not curable by radiation:

The silicone resins used in examples 1 and 2 are commercial methyl phenyl silicone resins (commercial product REN 60), which can be obtained as a 60% solution in xylene/toluene. To obtain solvent-free bonding agents, the solutions were combined with dipropylene glycol diacrylate and the solvent mixture (xylene/toluene) was distilled off qualitatively, so that a solution of methyl phenyl silane resin of dipropylene glycol diacrylate of the weight ratio 60:40 was obtained.

Example 1

The following components were mixed together for the manufacture of a radical-polymerizable clear coating agent:

	Monoester of hydroxyethylacrylate with phosphoric acid	1.0 % wt.
	3-Glycidyloxypropyl trimethoxysilane	3.0 % wt.
	Photoinitiator: 1-hydroxy-cyclohexyl-phenyl ketone	4.0 % wt.
5	Methyl phenyl silicone resin	10.0 % wt.
	Dipropylene glycol diacrylate	32.0 % wt.
	Tripropylene glycol diacrylate	27.0 % wt.
	Ethylene oxide/propylene oxide trimethylolpropane triacrylate (oligotriacrylate, molecular weight 480)	15.0 % wt.
10	Pentaerythritol tetraacrylate	7.0 % wt.
	Conventional defoaming agent	0.5 % wt.
	Silicone oil	0.5 % wt.

15 Example 2

Manufacture of a radical-polymerizable white coating agent

The following components were mixed together:

20	Monoester of hydroxyethylacrylate with phosphoric acid	2.0 % wt.
	γ -Glycidyloxypropyl triethoxysilane	4.0 % wt.
	Benzophenone	0.5 % wt.
	Photoinitiator: 2-hydroxy-2-methyl-1-phenyl-propan-1-one	2.5 % wt.
25	Photoinitiator: diphenyl-2,4,6-trimethyl-benzoyl-phosphane oxide	3.0 % wt.
	Methyl phenyl silicone resin	15.0 % wt.
	Dipropylene glycol diacrylate	30.0 % wt.
	Ethylene oxide/propylene oxide trimethylolpropane triacrylate (oligotriacrylate, molecular weight 480)	25.0 % wt.
30	Titanium dioxide	16.0 % wt.
	Silicone oil	2.0 % wt.

The following examples 3 to 5 describe the use of tri and/or polyfunctional (meth)acrylates:

35 Example 3

Manufacture of a radical-polymerizable red coating agent

40 The following components were mixed together:

	3-Glycidyloxypropyl trimethoxysilane	5.0 % wt.
	Monoester of hydroxyethylacrylate with phosphoric acid	5.0 % wt.
	Photoinitiator: 1-hydroxy-cyclohexyl-phenyl ketone	2.0 % wt.
45	Photoinitiator: benzophenone	3.0 % wt.
	Hexanediol diacrylate	20.0 % wt.
	Conversion product of hydroxyacrylates with a mixture of dicarboxylic anhydrides (phthalic anhydride, tetrahydrophthalic anhydride, succinic anhydride)	44.0 % wt.
50	Tripropylene glycol diacrylate	12.0 % wt.
	Saturated polyester from a mixture of multivalent polyalcohols and adipic acid, functionalized with acrylic acid	5.0 % wt.

Example 4

Manufacture of a radical-polymerizable black coating agent

5 The following components were mixed together:

	γ -Glycidyloxypropyl triethoxysilane	3.0 % wt.
	Monoester of hydroxyethylacrylate with phosphoric acid	7.0 % wt.
	Photoinitiator: 2-hydroxy-2-methyl-1-phenylpropan-1-one	4.0 % wt.
10	Saturated polyester from a mixture of multivalent polyalcohols and adipic acid, functionalized with acrylic acid	22.0 % wt.
	Hexamethoxymethylamine, partially etherized with hydroxyacrylates	10.0 % wt.
	Hexanediol diacrylate	14.0 % wt.
15	Trimethylolpropane triacrylate	20.0 % wt.
	Mixture of cycloaliphatic and aliphatic epoxide acrylates, monomer-free	15.0 % wt.
	Slip agent (silicone oil)	1.0 % wt.
20	Carbon black	4.0 % wt.

Example 5

Manufacture of a radical-polymerizable colorless coating agent

25 The following components were mixed together:

	Conversion product of hydroxyacrylates with a mixture of dicarboxylic anhydrides (phthalic anhydride, tetrahydrophthalic anhydride, succinic anhydride)	35.0 % wt.
30	3-Glycidyloxypropyl trimethoxysilane	5.0 % wt.
	Monoester of hydroxyethylacrylate with phosphoric acid	7.0 % wt.
	Photoinitiator: 1-hydroxy-cyclohexyl-phenyl ketone	5.0 % wt.
35	Urethanized polyacrylate, mixture of multivalent polyalcohols, converted with aliphatic diisocyanate hydroxyacrylate adducts	20.0 % wt.
	Dipropylene glycol diacrylate	8.0 % wt.
	Trimethylolpropane triacrylate	15.0 % wt.
	Silicone oil (slip agent)	2.0 % wt.
40	Silicone-modified acrylate (slip agent)	3.0 % wt.

Example 6

Manufacture of a cation-polymerizable blue coating agent

5 The following components were mixed together:

	Epoxide resin based on 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate containing 2 epoxide groups per molecule	50.0 % wt.
10	Addition product of polycaprolactone polyol to 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate	20.0 % wt.
	Hexanediol diglycidyl ether	20.0 % wt.
	3-Glycidyloxypropyl trimethoxysilane	5.0 % wt.
	Triarylsulfonium hexafluorophosphate (photoinitiator)	3.0 % wt.
15	Slip additive	1.0 % wt.
	Zappon blue	1.0 % wt.

Example 7

20 Manufacture of a radical-polymerizable colorless coating agent

The following components were mixed together:

25	Epoxide resin based on 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate containing 2 epoxide groups per molecule	40.0 % wt.
	Epoxide resin based on bisphenol A (Epicote 828)	20.0 % wt.
	Butanediol diglycidyl ether	20.0 % wt.
	OH-functional copolymer based on styrene allyl alcohol, OH number 188	10.0 % wt.
30	3-Glycidyloxypropyl trimethoxysilane	1.0 % wt.
	Triarylsulfonium hexafluorophosphate (photoinitiator)	3.0 % wt.

35 The coatings described above as examples in examples 1 to 7 were used in a device as described in Figure 1 for coating glass bottles. Odor-free, completely cured colored and clear bottles were obtained.

Claims

- 40 1. Process for the manufacture of coated glass hollowware by application of a radical-polymerizable coating and subsequent curing of the formed coating with high-energy radiation, characterized by the fact that it is carried out on-line, wherein the glass hollowware produced from a glass melt is subjected to a cold end coating, sorted and then immediately coated with a solvent-free, radical-polymerizable and/or cation-polymerizable coating in a coating thickness of at least 8 μm , whereupon the formed coating is cured by high-energy radiation and then exposed to a stream of air.
- 45 2. Process according to Claim 1, characterized by the fact that the air-blasting takes place with air of room temperature.
- 50 3. Process according to Claim 1, characterized by the fact that the air-blasting first takes place with hot air of 100 to 400°C and then with air of room temperature until the glass hollowware has cooled to a temperature of 40°C or below.
- 55 4. Process according to one of the preceding claims, characterized by the fact that a hot end coating of the glass hollowware takes place before the cold end coating.

5. Process according to one of the preceding claims, characterized by the fact that the application and curing of the coating takes place without protective gas atmosphere.
6. Process according to one of the preceding claims, characterized by the fact that the coating is applied by spray application with recycling of the overspray.
7. Process according to Claim 6, characterized by the fact that the spray application takes place in high-grade steel spray booths and that the overspray in the solvent-free coating is caught and recycled.
8. Process according to one of the preceding claims, characterized by the fact that a cold end coating based on polyethylene glycol fatty acid esters is used as cold end coating agent.
9. Process according to Claim 8, characterized by the fact that a cold end coating agent based on polyethylene glycol fatty acid esters is used, which additionally contains one or more silanes.
10. Process according to Claim 9, characterized by the fact that glycidyl group-containing silanes are used as silanes.
11. Process according to one of the preceding claims, characterized by the fact that UV radiation is used as the high-energy radiation for the curing.
12. Process according to one of the preceding claims, characterized by the fact that bottles are coated as glass hollowware.
13. Radiation-curable solvent-free radical-polymerizable coating, suitable for the coating of glass hollowware, containing
 - A) 1 to 10 %wt. of one or more silanes,
 - B) 1 to 10 %wt. of one or more monophosphates or diorganophosphates or triorganophosphates,
 - C) 2 to 10 %wt. of one or more photoinitiators and
 - D) as the remainder to 100 %wt., di(meth)acrylates, tri(meth)acrylates and/or higher-functional (meth)acrylates in the form of monomers, oligomers and/or polymers or mixtures thereof, optionally together with monoacrylates and/or silicone resins, as well as
 - E) optionally additional conventional varnish additives, dyes and/or pigments, wherein the parts by amount of lower and higher-molecular portions are selected so that the total composition has spray viscosity.
14. Coating according to Claim 13, containing in addition to 1 to 10 %wt. of component A), 1 to 10 %wt. of component B) and 2 to 10 %wt. of component C)
 - 5 to 30 %wt. of one or more nonradiation-curable silicone resins dissolved in the other components and as the remainder up to 100 %wt. the component D), as well as E) optionally conventional varnish additives, dyes and/or pigments.
15. Coating according to Claim 13, containing in addition to 1 to 10 %wt. of component A), 1 to 10 %wt. of component B) and 2 to 20 %wt. of component C)
 - 5 to 40 %wt. of one or more di(meth)acrylates,
 - 5 to 40 %wt. of one or more tri and/or polyfunctional (meth)acrylates and
 - 0 to 20 %wt. of one or more mono(meth)acrylates,
 - wherein the preceding components add up to 100 %wt., as well as E) optionally conventional varnish additives, dyes and/or pigments.
16. Radiation-curable, solvent-free cation-polymerizable coating suitable for the coating of glass hollowware, containing
 - 10-80 %wt. of one or more epoxide resins based on cycloaliphatic diepoxides containing at least two epoxide groups per molecule;
 - 5-50 %wt. of one or more liquid polyols having at least two OH groups per molecule, as softener;

5-50 %wt. of one or more liquid diglycidyl ethers as reactive thinning agent;

5-30 %wt. of one or more epoxide resins based on bisphenol A;

1-20 %wt. of one or more copolymers of styrene having α,β -olefinically unsaturated monomers,

1-5 %wt. of one or more photoinitiators and

5 1-5 %wt. of one or more silanes,

wherein the preceding components add up to 100 %wt. and the coating can additionally contain conventional varnish additives, dyes and/or pigments.

- 10 17. Process according to one of the Claims 1 to 12, characterized by the fact that it is carried out with a coating according to one of the Claims 13 to 16.
18. Use of the coating according to one of the Claims 13 to 16 for the coating of glass hollowware, especially of bottles.
- 15 19. Apparatus for the coating of glass hollowware open on one side, suitable for carrying out the process according to one of the Claims 1 to 12, with equipment for the melting of glass, manufacture of glass hollowware, hot end coating, cooling, cold end coating and sorting of the obtained glass hollowware, characterized by the fact that it has equipment for picking up glass articles at their open end and for feeding the glass articles in a suspended manner with their opening at the top, an encapsulated spray chamber of high-grade steel with equipment for high-temperature aftertreatment and then equipment for the take-off of the glass hollowware, connected in series immediately after the sorting equipment, wherein equipment for air-blasting with cold air can be connected between the encapsulated UV drying chamber and the equipment for the take-off of the glass hollowware or after the equipment for the take-off of the glass hollowware.
- 20 20. Apparatus according to Claim 19, characterized by the fact that it has equipment for the direct discharge of glass hollowware from the equipment for their pick-up and feeding before the equipment for the take-off of the glass hollowware and/or between the spray chamber and the UV drying chamber and/or between the UV drying chamber and the equipment for the high-temperature aftertreatment.
- 30 21. Apparatus according to Claim 19 or 20, characterized by the fact that the spray booth has a wet irrigation zone for the wet separation of overspray, which is fed by a circulating line for the coating equipped with pump and optionally filters.
- 35 22. Apparatus according to Claim 21, characterized by the fact that the spray booth is equipped with a second circulating line for the coating, equipped with pump and optionally filters, for the recycling to the spray equipment.
- 40 23. Apparatus according to one of the Claims 19 to 22, characterized by the fact that the equipment for the high-temperature aftertreatment is a hot air blower.